



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : B01D 15/00, C11B 3/10 C10G 25/00, B01J 20/12 C01B 33/21	A1	(11) International Publication Number: WO 92/06758 (43) International Publication Date: 30 April 1992 (30.04.92)
(21) International Application Number: PCT/GB91/01736 (22) International Filing Date: 7 October 1991 (07.10.91) (30) Priority data: 9022472.6 17 October 1990 (17.10.90) GB (71) Applicant (for all designated States except US): LAPORTE INDUSTRIES LIMITED [GB/GB]; 3 Bedford Square, London WC1B 3RA (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : TAYLOR, Roger, Skelton [GB/GB]; 26 Bembridge Close, Upton Bridle Path, Widnes, Cheshire WA8 9AA (GB). DAVIES, Mary, Elisabeth [GB/GB]; 41 St. Bridgets Close, Warrington, Cheshire WA2 0EW (GB). WILLIAMS, John [GB/GB]; 63 Clipsley Lane, Haydock, St. Helens, Merseyside WA11 0UE (GB).		(74) Agent: FFRENCH-LYNCH, C.; Group Patent Department, Laporte Industries Limited, Moorfield Road,, Widnes, Cheshire WA8 0JU (GB). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), JP, LU (European patent), NL (European patent), NO, SE (European patent), US. Published <i>With international search report.</i>
(54) Title: REMOVAL OF POLYAROMATIC HYDROCARBONS FROM LIQUIDS (57) Abstract <p>Polyaromatic hydrocarbons, such as benzo(a)pyrene, are removed from aqueous or organic liquids, such as edible oils or solutions or dispersions thereof, by the use of an organoclay absorbent, the clay having interlayer cation exchange capacity and the organic moiety being one or more onium cations occupying at least some of that cation exchange capacity and containing cyclic organic groups containing conjugated double bonds, the grouping being directly bonded to the central onium atom. Preferably the onium cation contains at least 1 lower alkyl grouping. Particularly preferred onium cations are the phenyltrimethylammonium or the 2,2,diphenylpropyl ammonium cations of which the latter provides a new organoclay. Residual contents of benzo(a)pyrene in oil below 1 ppb may be achieved.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LJ	Liechtenstein	SU ⁺	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE*	Germany	MC	Monaco	US	United States of America
DK	Denmark				

⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

Removal of polyaromatic hydrocarbons from liquids

This invention relates to the removal of polyaromatic hydrocarbons from oil or other liquids by adsorption onto a solid substrate.

Vegetable, animal or fish oils are produced on a large scale for human consumption. The production process, in the case of vegetable oils, may include drying of the source material, for example coconut flesh, by direct contact with flue gases or using open fires. This can cause the contamination of the oils with small but significant quantities of polyaromatic hydrocarbons. In the case of animal or fish oils similar contamination can occur due to pollution by discharged aqueous industrial effluents via the food chain. The term animal oil is used herein to include animal fats in liquid form.

Polyaromatic hydrocarbons are compounds comprising a plurality, that is three or more, fused aromatic rings. Some of these compounds, notably benzo(a)pyrene, are known or suspected carcinogens and it is desirable to reduce their concentration in oils or in aqueous liquids such as the industrial wastes referred to above. Benzo(a)pyrene is often present in about 10% of the total quantity of polyaromatic hydrocarbons and its removal is taken to be an indicator of the concomitant removal of other polyaromatic hydrocarbons. The removal of benzo(a)pyrene may be monitored by reverse phase HPLC analysis using a calibration curve obtained from prepared standard solutions. The benzo(a)pyrene may be eluted in hexane on an alumina column

SUBSTITUTE SHEET

and evaporated to dryness to provide a sample for analysis using a fluorimetric detector.

United States Patent Specification No. 4916095 discloses the removal of benzo(a)pyrene from waste water streams by the use of a clay having organic surfactant cations irreversibly bound to the surface. When the clay is an expansible clay, such as a swelling bentonite, it is first reacted with highly charged inorganic cations such as hydroxy aluminium polymeric 7^+ cations, which bind strongly to the interlayer cation exchange sites of the clay. A subsequent treatment with the cationic surfactant acts to cause irreversible binding of the surfactant only on the surface of the clay. Such inorgano-organoclays are effective to reduce the benzo(a)pyrene content of water. Cetyl pyridinium chloride-montmorillonite is taught in United States Patent Specification No. 4916095 to be suitable for the absorption of organic wastes from water, is shown to have activity in relation to chlorinated biphenyl or octachlorodioxin but to have little effectiveness in relation to fluorene or pentachlorophenol and was not tested in relation to benzo(a)pyrene.

According to the present invention polyaromatic hydrocarbons are removed from oils or other liquids by contact with organoclays bearing certain onium cations.

The present invention provides a process for reducing the content of polyaromatic hydrocarbons in liquids comprising contacting the liquid with an organoclay in which at least some of the interlayer cation exchange capacity is occupied by organic onium cations having the general formula:



where

X represents an atom of nitrogen, phosphorus, antimony or arsenic having a valency of 4 or of oxygen, selenium, sulphur or tin having a valency of 3

SUBSTITUTE SHEET

H represents one or more hydrogen atoms

R represents one or more organic radicals comprising a cyclic group containing conjugated double bonds which is directly bonded to the atom X,

n and m each represent numbers,

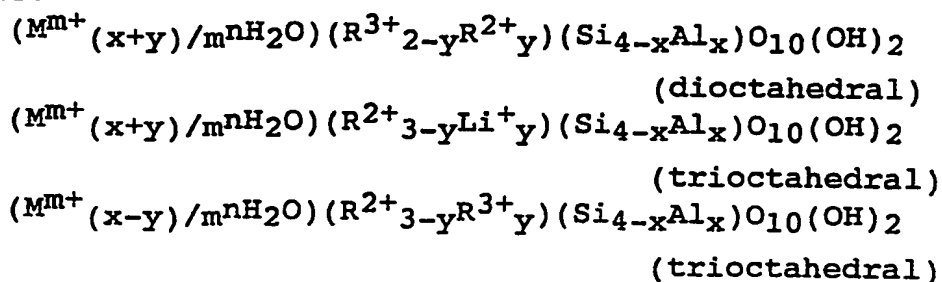
n + m is a number equal to the valency of X, m optionally representing zero.

Preferably X is a nitrogen atom or a phosphorus atom to give an ammonium or phosphonium cation.

One of the valencies of the atom X will be a delta bond involving two electrons.

The clays suitable for use according to this invention are layered materials capable of binding an onium compound by ion-exchange such as a silicate, aluminosilicate, aluminophosphate or like material the layers of which have acquired an anionic charge by the replacement of some framework Si, Al or P atoms by atoms of lower valency. Preferably the adsorbent is a smectite clay mineral or a synthetic analogue of such a mineral since these materials generally have a high cation exchange capacity of from about 50 to 150 m.eq/100 g.

Smectite minerals may be defined as a group of minerals or phyllosilicates of the 2:1 layer type with the general formulae:



where M^{m+} represents exchangeable cations such as Ca^{++} , Mg^{++} , having a valency m, necessary to satisfy the negatively charged lattice, R^{2+} represents magnesium or iron and R^{3+} represents aluminium or iron. The smectite group of minerals includes the mineral sub-groups montmorillonite,

SUBSTITUTE SHEET

beidellite, nontronite, saponite, hectorite and sauconite. Minerals belonging to the montmorillonite (dioctahedral), saponite or hectorite (trioctahedral) groups are particularly preferred for use according to the present invention. Fullers earth, is a montmorillonite containing predominantly Ca^{++} and Mg^{++} exchangeable cations which is suitable for use according to the present invention.

The ion-exchange binding of the onium cation with the anionic layered adsorbent may be achieved by treating the adsorbent substrate with a solution or suspension of the onium compound in water or other polar solvent.

The cation exchange capacity of the substrate is preferably saturated with the onium cations. To attain this the onium cation is preferably used in excess over the cation exchange capacity of the substrate. A suitable quantity of onium cation is above 1.0 but preferably 1.5 to 2.5 times the cation exchange capacity of the substrate. The substrate is preferably treated at a concentration of, for example, from 1 to 12% by weight with the onium cation. It is an important factor in achieving an efficient adduction that the substrate be in a highly dispersed state. The presence of shear assists dispersion and a suitable way of attaining this is by means of a high shear stirrer. Additionally a dispersion agent, such as tetrasodium pyrophosphate, may be included in the suspension. The quantity of dispersing agent may be suitably in the range of 0.1% to 5% and preferably from 1% to 4% by weight of the substrate. If any aggregates of substrate remain undispersed it may be desirable to remove such aggregates by, for example, centrifugation. The onium cation may be added to the dispersion of the substrate or may itself be dispersed at, for example, a concentration of from 1% to 6% by weight, and the two dispersions may be mixed while slowly adding the suspension of the onium compound to the dispersion of the substrate. Preferably the dispersion of the substrate and the mixed dispersions are

SUBSTITUTE SHEET

maintained under shear throughout, and for a sufficient time after the mixing has been completed to allow the cation exchange to go to completion. A suitable time is for 20 to 120 minutes after mixing has been completed. Preferably the temperature is maintained throughout at from 10°C to 90°C depending on the thermal stability of the onium cation.

The derivative resulting from the cation exchange may be filtered and washed free of inorganic cations from the substrate and anions associated with the onium cation. Again depending on the thermal stability of the onium cation it may be necessary to control the temperature of drying carefully to avoid decomposition of the onium cation.

The selection of the organic groups which are present on the onium cation is an important feature of this invention since this greatly influences the degree of adsorption of polyaromatic hydrocarbons from oil. The Applicants have found that some onium cations have substantially no effect but, after substantial research effort, have formulated guidelines for the selection of suitable onium compounds.

According to the present invention, the onium compound contains one or more cyclic groups containing conjugated double bonds, for example phenyl or substituted phenyl groups, directly connected to or incorporating the atom X of the onium cation. It is preferred that some of the groups R in the above stated formula are not the group containing conjugated bonds but are, for example, aliphatic groups containing from 1 to about 20 carbon atoms. It is preferred that one only at most of the groups R comprises a carbon-carbon chain containing more than 5, for example 6 to 20, carbon atoms, for example the hexadecyl group. Preferably 1 or 2 of the non-aromatic groups is an alkyl group containing from 1 to 5 carbon atoms. It is further envisaged according to this invention that the group containing the conjugated double bonds may very suitably be a polyaromatic group, for

SUBSTITUTE SHEET

example a naphthalene group. Alternatively, according to the invention, further aromatic groups may be connected to the aromatic group R or R^1R^2X via a linking group such as a methylene group or a polymethylene group.

The Applicant envisages that the electron density in the one or more cyclic groups R containing conjugated double bonds may be reduced by attraction to the onium atom X and that this may alter the character of the said cyclic groups to give them a greater affinity for the polyaromatic hydrocarbon atom which it is desired to adsorb. Thus a grouping containing fused conjugated double bond rings such as a pyrene grouping or a benzo(a)pyrene grouping when introduced into an onium compound and ionically bonded via the onium compound to a substrate may be an effective preferential adsorbent for benzo(a)pyrene contained in oils.

The treatment of a liquid containing polyaromatic hydrocarbons according to this invention may be carried out by contacting the liquid with a body of the organoclay suitably, for example, by passing the liquid through a column or bed of the organoclay or by mixing the organoclay into a body of the liquid in each case allowing sufficient contact time to achieve adsorption of the polyaromatic hydrocarbon onto the organoclay. An oil may be treated as such or in miscellar or solution form in a suitable solvent.

The present invention will now be illustrated by the following examples which are not limitative in any way on the scope of the invention. In these examples the abbreviation "Ph" is used to indicate the phenyl radical and "Pyr" the pyridinium radical.

SUBSTITUTE SHEET

Examples 1 to 9

The adsorbent was a Peruvian smectite clay having a cation exchange capacity of 50 to 100 m.eq/100 g. This clay was treated at ambient temperature with double its cation exchange capacity of the onium cation identified in the following Table in the form of a solution in water or ethanol. After 60 minutes the product was water washed and oven dried at 60-80°C.

A number of volumes (10ml) of a poor quality coconut oil containing 12.1 (± 1.0) ppb (parts per 10^9) of benzo(a)pyrene were treated with 0.5g of the onium exchanged adsorbent with stirring for 35 minutes at 100°C temperature. The adsorbent was then removed and filtered from the oil which was then analysed for residual benzo(a)pyrene. The quantity of benzo(a)pyrene adsorbed was assumed to equate to the difference between the original quantity and the residual quantity.

The results are summarised in the following Table.

Ex No	Onium Cation	Adsorbed B(a)P(ppb)	Residual B(a)P(ppb)	% wt B(a)P adsorbed
1	Phenyltrimethylammonium [Ph(Me) ₃ N ₊]	6.9	5.2	57.0
2	Tetraphenylphosphonium [(Ph) ₄ P ₊]	3.0	9.1	24.8
3	Tetramethylammonium [(CH ₃) ₄ N ₊]	0	12.0	0

SUBSTITUTE SHEET

Ex No	Onium Cation	Adsorbed B(a)P(ppb)	Residual B(a)P(ppb)	% wt B(a)P adsorbed
4	Tetraethylammonium [(CH ₃ .CH ₂) ⁴ N ₊]	0	11.9	0
5	Tetrapropylammonium [(CH ₃ .CH ₂ .CH ₂) ₄ N ₊]	0	13.2	0
6	Cetyltrimethylammonium {[CH ₃ (CH ₂) ¹⁵][CH ₃] ₃ N ₊ }	2.9	9.2	23.8
7	Benzyltrimethylammonium [(PhCH ₂)(CH ₃) ₃ N ₊]	1.8	10.3	14.9
8	4-nitrobenzyltrimethyl- ammonium [O ₂ NPhCH ₂)(CH ₃) ₃ N ₊]	0	12.5	0
9	1-(3-Nitrobenzyloxymethyl) Pyridinium [Pyr-CH ₂ -O-CH ₂ PhNO ₂]	1.4	10.7	11.6

Example 1 is according to the invention.

In Examples 3 to 5 the organoclay contained no groups containing conjugated double bonds. In Example (9) the organoclay contained 4-valent nitrogen in pyridinium, not ammonium, form. In Examples 7 and 8 the group containing conjugated double bonds was connected to the nitrogen atom via a methylene group i.e. was not directly connected to the nitrogen atom. In Example 2 there were no non-aromatic substituents as is preferred according to the invention. In Example 3 there were no short chain alkyl groups as is preferred according to the invention.

A further series of tests was conducted on the

SUBSTITUTE SHEET

treatment of a poor quality coconut oil containing 4.8 ppb of benzo(a)pyrene. In Examples 10-20 set out below the clay was varied but the onium cation, phenyltrimethylammonium, remained constant. In each of examples 10 to 16 the oil was treated with a standard dosage of 5% by weight of the organoclay while in Examples 17 to 20 the quantity of organoclay was reduced to 4.0, 2.0, 1.0 and 0.5% wt respectively.

Ex No	Clay	B(a) P adsorbed	
		ppb	%
10	Spanish calcium montmorillonite	4.0	83.3*
11	as above but acid activate	3.9	81.2
12	Sepiolite	3.5	72.9
14	as Ex 13 but acid activated	1.2	25.0
15	Attapulgite/montmorillonite	2.9	60.4
16	Synthetic hectorite	2.6	54.2
17	Spanish calcium montmorillonite (4%)	3.8	79.2
18	" " " (2%)	2.9	60.4
19	" " " (1%)	2.2	45.8
20	" " " (0.5%)	1.3	27.1

(* residual B(a) P content 0.8 ppb)

It is seen that non-smectite clays give reduced performances, that calcium montmorillonite gave the best performances and that it is necessary to ensure that a sufficient clay dosage is used to achieve optimum performance. In further tests (Examples 21-23) the same oil and the dosage used in Examples 10-16 was used and the clay was Spanish calcium montmorillonite but the onium cation was varied.

SUBSTITUTE SHEET

Ex No	Cation	B(a)P adsorbed	
		ppb	%
21	2,2 diphenyl propylamine (Ph) ₂ C ₃ H ₇ N ⁺ H	3.5	72.9
22	Cetyltriphenylphosphonium (Ph) ₃ P ⁺ (CH ₂) ₁₅ CH ₃	0.7	14.6
23	benzylviologen [Ph-CH ₂ -pyr-] ₂	1.0	20.8

Example 21 is according to the invention. In Example 22 there is no short chain alkyl group as is preferred and in Example 23 the 4-valent nitrogen atom is in pyridinium form. 2,2 diphenyl propylamine is a new compound.

SUBSTITUTE SHEET

Claims

1. A process for reducing the content of polyaromatic compounds in liquids comprising contacting the liquid with an organoclay in which at least some of the interlayer cation exchange sites of the clay are occupied by organic onium cations, the process being characterised in that the cations have the general formula $R_nXH_m^+$ wherein X represents an atom of nitrogen, phosphorus antimony or arsenic having a valency of 4 or of oxygen, selenium, sulphur or tin having a valency of 3, H represents the hydrogen atom, R represents an organic radical comprising a cyclic group containing conjugated double bonds which is directly bonded to the atom X, n and m each represent members the sum of which equals the valency of X, m optionally representing zero.
2. A process as claimed in claim 1 wherein X represents an atom of phosphorus or of nitrogen.
3. A process as claimed in claim 1 or 2 wherein the onium cation contains one or more alkyl groups containing up to 20 carbon atoms.
4. A process as claimed in claim 3 wherein not more than 1 of the alkyl groups contains more than 5 carbon atoms.
5. A process as claimed in claim 4 wherein 1, 2 or 3 of the alkyl groups contains from 1 to 5 carbon atoms.
6. A process as claimed in any preceding claim wherein the onium cation contains one or more phenyl or substituted phenyl groups.

SUBSTITUTE SHEET

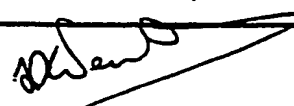
7. A process as claimed in any preceding claim wherein the onium cation contains a grouping containing fused conjugated double bond rings.
8. A process as claimed in any preceding claim wherein the cation exchange capacity of the clay is substantially saturated with onium cations.
9. A process as claimed in any preceding claim wherein the clay has a cation exchange capacity of from 50 to 150 meq/100 g.
10. A compound containing an onium cation and being suitable for the production of an organoclay which compound is 2,2 diphenyl propylamine.
11. An organoclay suitable for use to reduce the content of polyaromatic compounds in liquids wherein the organic moiety is an onium cation as claimed in claim 10.
12. A process as claimed in any one of claims 1 to 9 wherein the liquid to be contacted with the organoclay is an oil.
13. An oil-purification adsorbent comprising an organoclay comprising a clay of which at least some of the interlayer exchange sites are occupied by organic onium cations having the general formula:
$$R_nXH_m^+$$
wherein X, H, R, n and m are defined in claim 1 or 2.
14. An organoclay adsorbent as claimed in Claim 13 wherein the onium cation and the clay are as further identified in any one of claims 3 to 9.

SUBSTITUTE SHEET

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 91/01736

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5	B01D15/00; C01B33/21	C11B3/10; C10G25/00; B01J20/12
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	B01D ; C11B ; C10G ; B01J C01B ; A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	WO,A,8 301 205 (RADIAN CORP.) 14 Apr 11 1983 see page 9, line 8 - page 16, line 5 ---	1-5
A	US,A,4 386 010 (HILDEBRANDT) 31 May 1983 ---	
A	EP,A,0 175 287 (HOECHST) 26 March 1986 ---	
A	GB,A,1 565 362 (LAPORTE IND.) 16 Apr 11 1980 see page 1, line 26 - page 3, line 7 ---	1-3
<p>¹⁰ Special categories of cited documents : ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
09 JANUARY 1992	16. 01. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	WENDLING J.P. 	

Form PCT/ISA/210 (second sheet) (January 1985)

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9101736
SA 51872**

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 09/01/92

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-8301205	14-04-83	AU-A- 8993582	27-04-83
		AU-A- 8999082	27-04-83
		AU-A- 8999482	27-04-83
		AU-A- 8999582	27-04-83
		CA-A- 1205389	03-06-86
		EP-A- 0090017	05-10-83
		EP-A,B 0090842	12-10-83
		EP-A,B 0091469	19-10-83
		EP-A- 0090027	05-10-83
		WO-A- 8301204	14-04-83
		WO-A- 8301206	14-04-83
		WO-A- 8301208	14-04-83
		US-A- 4473477	25-09-84
		US-A- 4470912	11-09-84
		US-A- 4517094	14-05-85
		US-A- 4549966	29-10-85
US-A-4386010	31-05-83	US-A- 4444665	24-04-84
EP-A-0175287	26-03-86	DE-A- 3434709	03-04-86
		CA-A- 1251440	21-03-89
		JP-A- 61078437	22-04-86
		US-A- 4742039	03-05-88
GB-A-1565362	16-04-80	None	

EPO FORM P0079

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82